Surfactant-assisted removal of swep residues from soil and photocatalytic treatment of the washing wastes

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ABSTRACT

The photocatalytic treatment of soil washing wastes containing the pesticide swep and three different surfactants: sodium dodecylsulfate (SDS), hexadecyltrimethylammonium bromide (HTAB) and polyoxyethylene(8) dodecyl ether ($C_{12}E_8$), has been investigated. Better extraction performances of swep (methyl-N-(3,4-dichlorophenyl)carbamate) from contaminated soil samples have been obtained using aqueous SDS solutions. The pesticide abatement in the wastes, performed by photocatalysis in the presence of irradiated TiO_2 dispersions, was faster in the presence of SDS and slower in the presence of HTAB, whereas a marked degradation inhibition was observed when $C_{12}E_8$ solutions were used. The monitoring of end products formation in water, together with a detailed MS examination of the transient intermediates formed during the earlier steps of the pesticide degradation, allowed to give insight into the process mechanism operating in aqueous media.

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1. Introduction

The intensive use of pesticides in agriculture practice frequently gives rise to the contamination of soil and water resources, thus suitable remediation techniques are applied in order to overcome or minimize the risks arising from the use of such products.

Among the pest control agents various N-aryl and N-methyl carbamates are widely applied as herbicides for the treatment of rice and various field crops, such as cotton and soybean. Generally these compounds, which act as inhibitors of photosynthesis and cell mitosis, exhibit a more or less relevant persistency in soils depending on their tendency to adsorb, in turn related to the pesticide structure. Persistencies up to ca. 3 months have been reported for the more hydrophobic carbamates [1]. Thus, in certain cases, the removal of pesticide residues from soils could be necessary.

Soil washing, a well known ex situ remediation technology, can be applied to remove organic pollutants from contaminated soils having a relatively small percent (<30–40%) of silt and clay fractions. The treatment is usually based on the use of aqueous surfactant solutions, exploiting both the lowering of the interface tension of the washing liquid and the solubilization capabilities of micellar aggregates [2–4].

Among the surfactants used for soil washing, nonionics are usually preferred on the basis of their very low critical micellar concentration (c.m.c.), which reduces the presence of residual surfactant on the washed solid [5]. On the other hand, anionic surfactants exhibit a lower tendency to adsorb onto the soil particles, but have higher c.m.c. values. In some cases the use of mixtures of these two types of surfactants has been proposed [6–8]. Cationic surfactants are generally less used since they tend to adsorb strongly onto the soil.

In all the cases, soil washing gives rise to the production of significant amounts of washing wastes, which must be successively disposed and/or treated.

In the past years increased attention has been devoted to the application of advanced oxidation processes (AOPs), in particular photocatalysis, to treat complex aqueous wastes [9–12]. This approach is interesting since it allows to convert most organic pollutants into harmless chemicals.

However, the feasibility of photocatalytic treatments of surfactant-containing aqueous wastes has to be carefully examined, since surfactants are themselves degraded [13] and their aggregation structures can largely influence the degradation of the target pollutants [14–16].

In this work we investigated the performances of different aqueous surfactant solutions, used as soil washing agents, to extract swep residues from contaminated soil samples. Successively, the possible application of heterogeneous photocatalysis to effectively remove the pesticide from the washing wastes was investigated by using TiO_2 dispersions under simulated sunlight irradiation.

The analysis of swep degradation in water, with particular attention devoted to the isolation and identification of the

transient products formed during the initial reaction steps, has also been performed in order to give insight into the process mechanism, which until now has not been examined in detail.

2. Experimental

2.1. Materials and methods

2.1.1. Soil samples

Clean soil samples, taken from a hill zone near Alba (Piedmont region, Italy), were sieved to <2 mm to remove the bigger particles and vegetable remnants and successively homogenized. The mean organic fraction content in such soils is typically around 2%.

The percent of water in these samples (2.6%) was determined using the EPA Method 345466: weighed amounts of soil and Na_2SO_4 (dried at 400 °C for 4 h) have been mixed and heated at 105 °C overnight; the loss weight after this treatment allows to estimate the percentage of humidity.

2.1.2. Reagents

Swep (purity 99.9%, Sigma–Aldrich) was used as received.

Polycrystalline TiO_2 Degussa P25 (composed of ca. 80% anatase and 20% rutile) was employed in all the photodegradation experiments. In order to remove any organic impurity this oxide was washed with water and irradiated under stirring with simulated solar light for about 12 h. The washed semiconductor was then dried in the oven at 80 °C. The resulting powder was resuspended in water by sonication immediately before use.

Methanol (Fluka)/water mixtures were used as LC eluents. Na_2CO_3, $NaHCO_3$ solutions (Merck) and metansulfonic acid (Merck) were used as eluents for the IC measurements.

NaOH and H_2SO_4 (Merck) were used to adjust the pH. The analytical-grade surfactants N-hexadecyl-N,N,N-trimethylammonium bromide (HTAB, Merck), sodium dodecyl sulfate (SDS, Merck) and polyoxyethylene(8) lauryl ether ($C_{12}E_8$, Nikkol) were used in soil washing experiments. Acetone and n-hexane (both from Aldrich) were employed for the exhaustive extraction of the soil samples. Pure water was produced using a Milli-QTM system (Millipore).

2.1.3. Instruments and methods

The substrate degradation was followed by HPLC, employing a Merck-Hitachi instrument, equipped with a L-6200 pump and UV–vis L-4200 detector. A column RP-C18 (Lichrospher, 4 mm i.d. × 125 mm long, from Merck) was used. The eluent was methanol/water 60/40% (v/v), flow rate 1.0 mL min^{-1}. The detector wavelength was 220 nm.

The formation of ionic degradation products was followed by a suppressed ion chromatography, employing a Dionex DX 500 instrument equipped with a conductimeter detector (ED 40, Dionex). The anions (nitrate and nitrite) have been analysed by using an AS9HC anionic column (Dionex) 200 mm long × 4 mm i.d. The elutions were performed at 30 °C, at a flow rate of 1 mL min^{-1} using an aqueous solution of K_2CO_3 (10 mM) and $NaHCO_3$ (4 mM).

The determination of ammonium ions was performed by employing a CS12A column (Dionex) 200 mm long × 4 mm i.d., using metansulfonic acid 25 mM as eluent, at a flow rate of 1 mL min^{-1}.

The evolution of the dissolved organic carbon (DOC) during the photocatalytic runs was followed using a Shimadzu 5000 TOC analyser (catalytic oxidation on Pt at 680 °C). Calibration runs were performed injecting known amounts of potassium phthalate.

The analysis of organic intermediates, arising from the initial steps of swep degradation, was performed by HPLC-MS. A Dionex Ultimate 3000 HPLC coupled with a Surveyor PDA UV detector and a LTQ Orbitrap mass spectrometer (Thermo Scientific) equipped with an atmospheric pressure interface and an ESI ion source was used. The LC column effluent was delivered into the ion source using nitrogen as sheath and auxiliary gas. The source voltage was set to 3.1 kV. The heated capillary temperature was maintained at 275 °C. The main tuning parameters adopted for ESI source were: capillary voltage −34.00 V, tube lens offset −68.57 V. Mass accuracy of recorded ions (versus calculated) was ±15 ppm (without internal calibration). The chromatographic separations were performed on a Phenomenex Luna 3 μm C18 (2) column, 150 mm × 2.0 mm, 3 μm particle size, thermostated at 30 °C. Injection volume was 20 μL and flow rate 200 μL min^{-1}. The following gradient mobile phase composition was adopted: acetonitrile/ammonium acetate 0.1 mM 20/80 to 100/0 in 40 min. MS and MS^n analyses were performed in the negative ions mode; the mass range was 50–350 Da.

2.2. Analytical procedures

2.2.1. Soil spiking

100 g of soil was treated with 100 mL of an acetone solution containing the pesticide. The concentration of swep was chosen in order to obtain a final concentration of ca. 20 mg L^{-1} in the washing solutions, near to its solubility limit in water (ca. 50 mg L^{-1}) [17].

The soil was mixed thoroughly with a magnetic stirrer for 1 h and then left unsealed overnight under hood to allow the solvent evaporation.

2.2.2. Soil washing experiments

All the washing runs were performed on 3.75 g of soil to which 25 mL of aqueous surfactant solution was added. The samples were placed in stopped tubes in a rotatory mixer (rotation speed: ca. 10 rpm). The standard contact time was 5 h.

The obtained soil dispersions were centrifuged at 5000 rpm for 10 min and aliquots of the supernatant clear solutions were filtered through 0.45 μm Millex LCR hydrophilic PTFE membranes (Millipore). The quantification of substrate has been performed by HPLC, as previously detailed.

2.2.3. Degradation experiments

The degradation experiments were carried out in a photochemical stirred batch reactor from Helios-Italquarz (Milan), equipped with a medium pressure mercury lamp (125 W). The Pyrex glass jacket surrounding the lamp acted as a cut-off filter for wavelengths shorter than 300 nm.

A series of preliminary photocatalytic runs were performed on 500 mL of solution containing ca. 17 mg L^{-1} of swep, 200 mg L^{-1} of dispersed TiO_2 and other additives, if necessary. The soil washing solutions were degraded in the presence of different amounts of semiconductor (200–1000 mg L^{-1}) and were kept saturated with bubbling air during the treatment. The temperature was 25 °C. Samples (5 mL) of irradiated dispersion were taken from the reactor at different times; all the analytical determinations were performed after filtration.

In order to ensure the quantitative recovery of the substrate, 5 mL of methanol were added to the samples taken during the degradation runs before the filtration.

3. Results and discussion

3.1. Soil washing performances

The extraction performances of three surfactants (HTAB, SDS and $C_{12}E_8$) were investigated. These surfactants were chosen on the basis of their non-aromatic nature, in order to reduce the

possible competition between the amphiphiles and the investigated soil pollutant during the photocatalytic treatment step.

Taking into account the c.m.c. and aggregation number data, surfactant concentrations were chosen in order to have initially nearly the same concentration (ca. 8.3×10^{-6} M) of micelles, assumed as macromolecules. The working concentrations of HTAB, SDS and $C_{12}E_8$ were 1.0×10^{-3} M, 8.6×10^{-3} M and 1.1×10^{-3} M, respectively. Measurements of surface tension of these surfactant solutions after contact with soil samples (and filtration through 0.45 μm filters) clearly indicated that the surfactant concentrations are still above the c.m.c. in all the cases.

After the established contact period (5 h) all the soil extracts showed a yellowish colour. The recovery yields are reported in Fig. 1. The percentages were calculated with respect to the recoveries obtained using the mixture acetone/hexane 50:50, v/v, in the same experimental conditions. The standard deviations, estimated from five replicated measurements, were in the range 5–8%.

It can be seen that SDS allows to obtain the higher recovery. The extraction results can be explained taking into account two mechanisms occurring in surfactant soil washing: the first one prevails below the critical micelle concentration (soil rollup mechanism), whereas the second one takes place above this concentration limit (solubilization) [18].
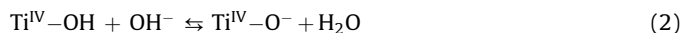
Anionic and nonionic surfactant are less likely to be adsorbed onto the soil and this leads to enhanced micelle formation in the washing solution, thus favouring a higher recovery of hydrophobic substrates. For cationic surfactants their adsorption onto soils takes place in two phases: initially via cation exchange and after by formation of double-layer and admicelles on the soil surfaces. The contaminant partition between these structures tends to reduce the remediation efficiency [19].

3.2. Photocatalytic degradation experiments

Before to start with the photocatalytic runs some blank experiments were performed in the dark, in the absence of TiO_2. No appreciable degradation of swep was observed after 2 h irradiation, thus confirming its photostability under the described working conditions.

The mechanism of photocatalysis, extensively investigated and reported in the literature [9–12], will be not examined here. Basically, the degradation of a wide number of organic substrates occurs through a multistep process involving the attack of organic molecules by reactive oxidizing species, in particular $^\bullet OH$, formed upon irradiation of the semiconductor particles. Protonation or deprotonation of surface hydroxy groups can occur depending on the solution pH.

$$Ti^{IV}-OH + H^+ \leftrightarrows Ti^{IV}-OH_2^+ \tag{1}$$

$$Ti^{IV}-OH + OH^- \leftrightarrows Ti^{IV}-O^- + H_2O \tag{2}$$

$$TiO_2 + h\nu \rightarrow TiO_2(e^-_{CB} + h^+_{VB}) \tag{3}$$

$$H_2O + h^+ \rightarrow {}^\bullet OH + H^+ \tag{4}$$

$$OH^-_{(ads)} + h^+ \rightarrow {}^\bullet OH \tag{5}$$

In addition to the oxidation paths, reduction processes involving the electrons in the conduction band could be also present in some cases [20].

Taking into account the nature of the examined pesticide and the properties of the employed semiconductor, the photocatalytic degradation was investigated at different initial pH values of the aqueous dispersions: 3.0, 5.6 and 8.0, which are below, in the range and above the isoelectric point of anatase [21], respectively.

Fig. 2 shows the evolution of the primary process as a function of the initial pH. As previously reported for most organic compounds, the swep degradation follows a pseudo-first order kinetic law, according to the equation:

$$\frac{-dC_{sub}}{dt} = k_{obs}C_{sub} \tag{6}$$

where C_{sub} is the substrate concentration and k_{obs} is the observed first-order rate constant. According to Eq. (6), linear plots of $\ln(C/C_0)$ versus time have been obtained up to ca. 70–80% swep degradation (see inset in Fig. 2).

The analysis of the primary process reveals a modest increase of the degradation rate with increasing initial pH. Taking into account that the protonation of the amido groups occurs in strong acidic media [22,23] and that deprotonation of swep is expected only at high pH values (a pK_a value around 14 is reported [24]), negligible repulsive effects between swep and semiconductor particles are expected within the investigated pH range. Thus, the observed modest increase in the reaction rate with increasing pH could be mainly attributed to the increased formation of OH radicals due to the improved transfer of holes to the adsorbed water and hydroxyls, according to Eqs. (4) and (5).

Although the photocatalytic degradation of various carbamic pesticides in water under different experimental conditions has been previously investigated, only one report [25] concerned swep and a lack of information still exists about the degradation mechanism of this pesticide in aqueous media. Our attention was
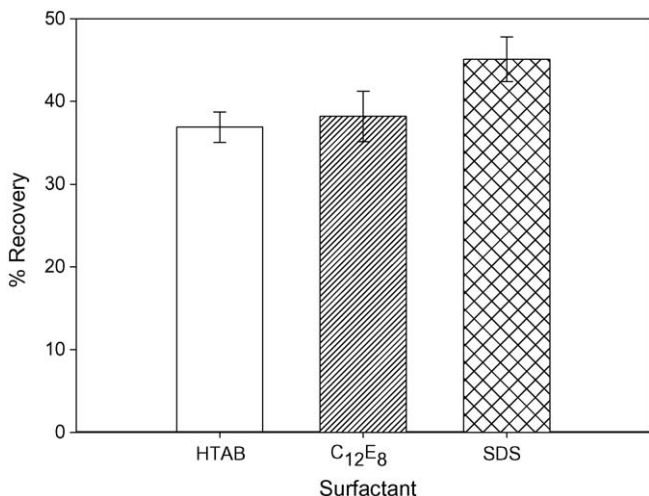

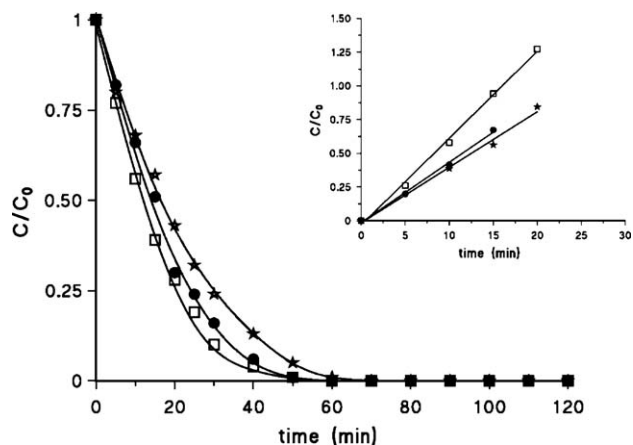**Fig. 1.** Recoveries of swep using the investigated surfactants.

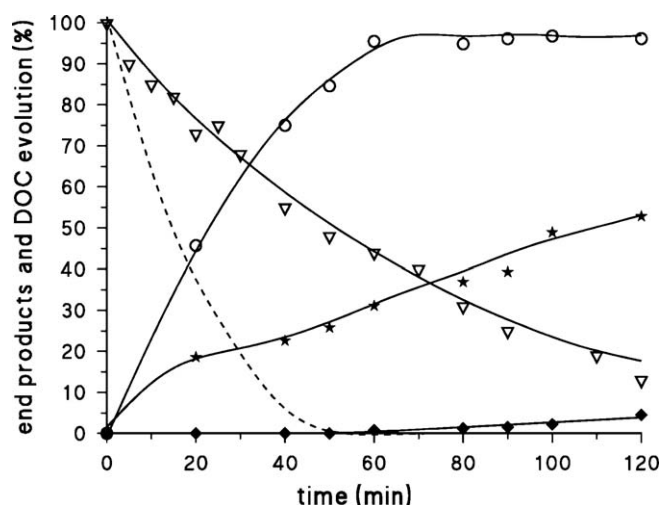**Fig. 2.** Effect of initial pH on swep degradation, pH 5.6 (●), 8 (□), 3 (★).

Fig. 3. Evolution of end products and DOC during the photocatalytic degradation of swep in the presence of 200 mg L^{-1} of TiO$_2$ (○ chloride, ▽ DOC, ◆ nitrate, ★ ammonium, dashed line: primary process).

thus focused on this point, with particular interest devoted to the MS characterization of organic transient intermediates formed during the initial degradation steps.

3.3. Analysis of the end products

The formation of the mineralization end products has been investigated at pH 5.6. Fig. 3 shows the decrease of dissolved organic carbon during the irradiation of aqueous solutions of pesticide in the presence of 200 mg L^{-1} of TiO$_2$.

A residual concentration of DOC (ca. 13% of the initial content) was found even after 120 min irradiation, indicating a slow

mineralization process. Taking into account that the complete disappearance of the pesticide occurs in a shorter time (ca. 60 min), the residual DOC can be attributed to the presence of organic intermediates [26–28,25]. Since the presence of aromatic derivatives was not detected by HPLC after 60 min irradiation, it can be reasonably attributed to compounds originated from the ring opening the organic carbon found in the solution at that time.

The evolution of chloride, nitrate and ammonium was reported in Fig. 3. It can be noted that the stoichiometric formation of Cl$^-$ is obtained after ca. 60 min irradiation, thus indicating that the pesticide dechlorination is much faster than its mineralization to CO$_2$.

No nitrite traces were detected under the employed experimental conditions, in agreement with previous results reported for other carbamates [27].

As far as the formation of NO$_3^-$ and NH$_4^+$ is concerned, we observed a continuous increase of their concentrations with increasing irradiation time. Ammonium was found to be the main nitrogen-containing end product and accounts for ca. 53% of the total nitrogen, after 120 min irradiation. At this time the nitrogen mass balance is lower than the stoichiometric value, thus indicating that organic nitrogen could be still present, probably in organic intermediates. However, the possible formation of hydroxylamine during the ammonia photooxidation over TiO$_2$ has also been hypothesized and further degradation of this product leads to the formation of gaseous N$_2$ and nitrogen oxides [29], which can be more easily lost.

3.4. Identification of transient intermediates formed in the earlier reaction steps

The investigation of the nature of organic intermediates was performed via HPLC–DAD–MS analysis on the irradiated solutions, previously concentrated up to 50 times. The samples were taken after 10 and 15 min irradiation, times at which the aromatic
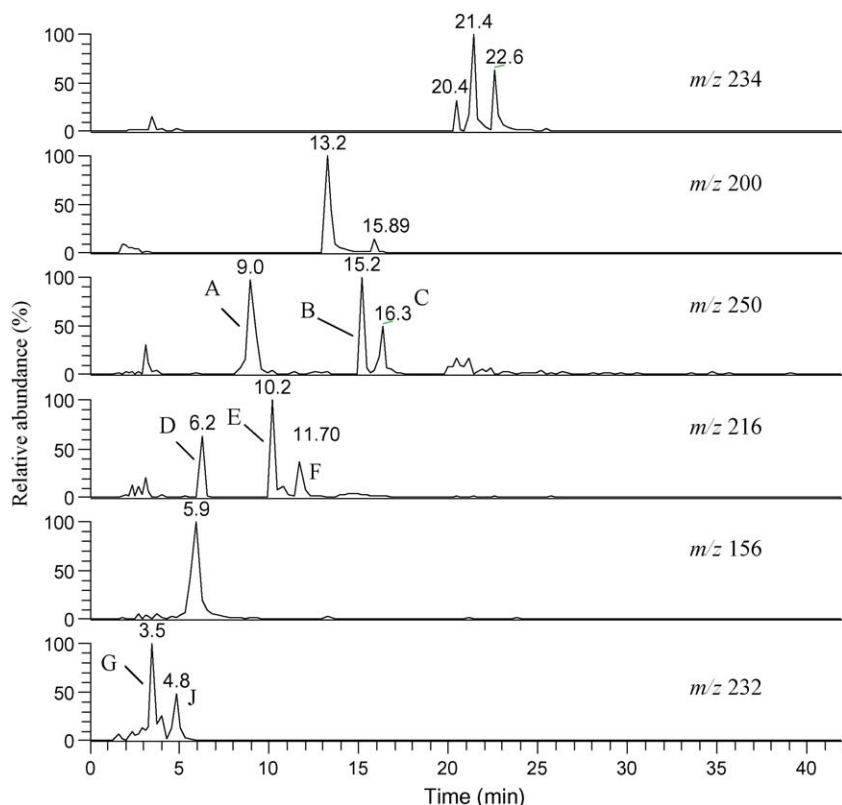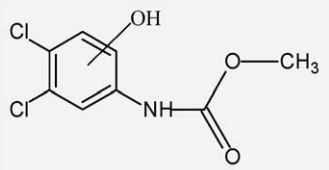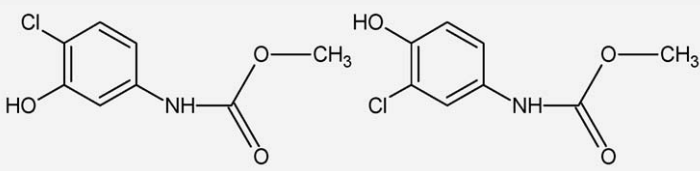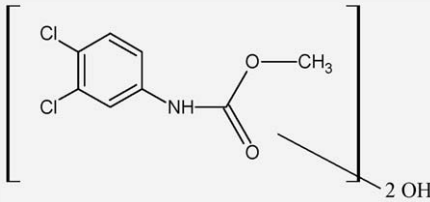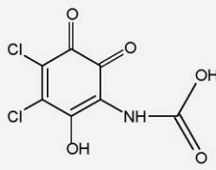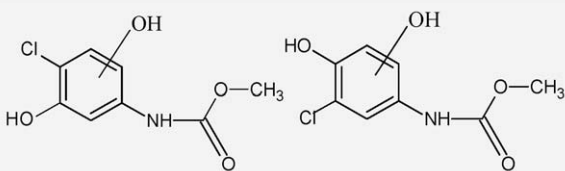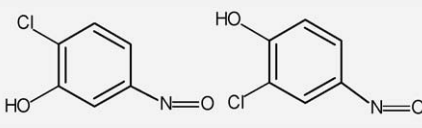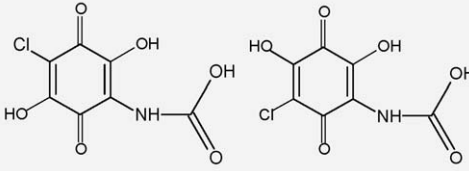

Fig. 4. LC–MS pattern of the swep sample after 10 min irradiation displayed at different m/z values. Initial pH 5.6.

Table 1
Swep degradation in water: intermediates detected after 15 min of irradiation.

Precursor ion (m/z)	Possible structures of the transient intermediates	t_R (min)
234		20.4 21.4 22.6
200		13.2 15.9
250		15.2 16.3
250		8.9
216		6.2 10.2 11.7
156		5.9
232		3.5 5.0

intermediates are still present at significant concentrations and can be better evidenced.

Fig. 4 shows different digital reconstructions, at various significant m/z values, of the chromatographic pattern of the sample, degraded at pH 5.6. Also the solutions irradiated at pH 3 and 8 showed similar profiles, thus supporting the hypothesis that pH mainly affects the swep abatement kinetics, whereas

the degradation mechanism seems to remain essentially the same.

The intermediates structures, reported in Table 1, have been proposed on the basis of the evidenced m/z values and considering the corresponding MS^n spectra fragmentation.

Three peaks with retention times shorter than swep have been found when extracting from the total ionic current the m/z 234;

this value, higher than that of the parent molecule, and the chromatographic behaviour are consistent with the hypothesis of the formation of mono hydroxylated products. The MS^2 spectra of these compounds present only a product ion at 202 m/z deriving from the neutral loss of the CH_3OH molecule. Taking into account that the fragmentation pathway of swep also showed this loss as main fragmentation, we can hypothesize the introduction of OH on one of the available positions of the aromatic ring.

In the MS^3 spectrum of m/z 202, the m/z 166 ion (−36 Da, assigned to HCl loss) is the most abundant fragment present for the three signals. Nevertheless the analysis of the spectrum did not provide useful information to discriminate between the three possible isomers.

For the intermediate with m/z 200, two peaks were detected. The isotopic profile shows the presence of only one chlorine atom in the structure, thus suggesting that the degradation path can lead to the simultaneous hydroxylation and dechlorination of the molecule, in agreement with the observed chloride evolution. The number of detected peaks is consistent with the two possible positions of substitution of Cl with OH group. However the more abundant formation or accumulation of only one of isomers (peak at t_R = 13.23 min) was observed. By an accurate MS^3 analysis, both signals show the formation of two fragment ions having m/z 168 and 141, due respectively to the neutral group loss of 32 (CH_3OH) and to a radical loss of 59 Da ($\bullet C_2H_3O_2$). The MS^4 fragmentation has been performed on both ions, but the observed loss of 36 (HCl) did not supply further information.

The formation of the above mentioned transient derivatives suggests that the ring hydroxylation, with or without the elimination of halogen atoms, is the main initial reaction step of the photocatalytic degradation of swep.

For the most abundant compounds having m/z 200 (t_R = 13.2 min) and m/z 234 (t_R = 21.4 min and t_R = 22.6 min), their formation and disappearance during the degradation treatment was followed by HPLC-UV at the three investigated initial pH values (see Fig. 5A–C). The analysis was directly performed on the irradiated solution, without preconcentration.

It can be seen that the evolution of the different peaks shows a typical bell-shaped profile. At pH 5.6 the intermediates formation is faster, reaching a maximum amount of intermediates formed after ca. 20 min irradiation. The complete degradation of the intermediates at this pH occurs after 50–60 min irradiation, whereas working at the other reported pH values, in particular at pH 3, a slower degradation rate of the transient intermediates is observed.

Concerning the other degradation products reported in Table 1, the key role of the HRMS was essential for the structure assignment of intermediates having m/z = 250; in fact among the three signals obtained, compound A has an accurate m/z value of 249.9274, whereas this value is equal to 249.9636 for compounds B and C.

Compounds B and C were identified as the substrate dihydroxyderivatives; their MS^2 spectra analysis show for both isomers the formation of a product ion at m/z 217.9287, due to the loss of CH_3OH. On the basis of the previous considerations, it is possible to propose the introduction of both OH groups on the ring. For compound A, the high resolution mass spectrum suggests the empirical formula: $C_7H_2O_5NCl_2$, which is compatible with the proposed structure reported in Table 1.

The MS^n analysis suggests a different fragmentation pattern in respect with the compounds B and C. The absence of CH_3OH loss and the presence of product ions at m/z 214 (−36 HCl) and 145 (radical loss of 105 Da $\bullet C_3H_2ClO_2$) are in agreement with the proposed structure.

Three species at m/z 216 were detected and labelled D, E, F. The mass difference (16 Da) in respect to the intermediate having m/z
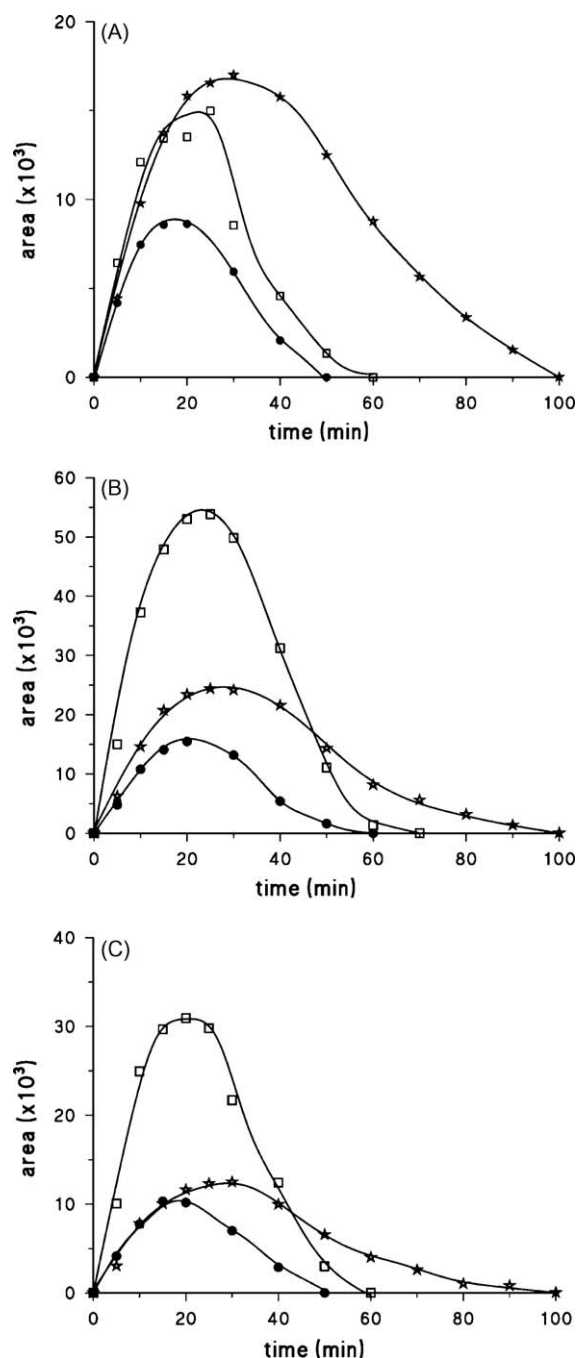

Fig. 5. Evolution of main intermediates formed from swep degradation as a function of the irradiation time. (A) m/z 200 (t_R = 13.2 min), (B) m/z 234 (t_R = 21.4 min) and (C) m/z 234 (t_R = 22.6 min). pH 5.6 (●), 8 (□), 3 (★).

200 allows us to hypothesize the introduction of a second OH group on the ring. The corresponding MS/MS spectra still exhibit the loss of 32 Da (signal at m/z 184), thus confirming the preferential OH attack on the aromatic moiety.

The formation of product ions having m/z 148 (−36 Da, HCl loss) and m/z 120 (−28 Da, CO loss) was observed in the MS^3 spectra performed on the ion at m/z 184; in all cases we can hypothesize the formation of three isomers coming from the introduction of a second OH group in each one of the three available positions on the ring.

In addition to intermediate A, a structure deriving from the partial degradation of the carbamic group was assumed for the compound with m/z 156.

Two signals were detected for m/z 232 value, although the first at $t_R = 3.5$ min is more abundant that the second, $t_R = 5$ min. The accurate mass value suggests an empirical formula of $C_7H_3O_6NCl$, which allows to hypothesize the structure shown in Table 1.

As reported for compound A with m/z 250, the corresponding MS^2 spectra did not show the typical loss of 32 Da observed for swep and its hydroxyderivatives; in particular for compound G a loss of 105 Da, corresponding to a loss of $C_3H_2ClO_2$ radical, was shown, whereas the formation of a product ion with m/z 188 was found for compound J, suggesting the loss of one CO_2 molecule.

Taking into account that only three intermediates are largely abundant, they can be considered as the initial products formed starting from the swep molecule. The sequence of events leading to the formation of the other detected compounds is more difficult to ascertain since these compounds are less abundant and, moreover, they can originate from different intermediates. On the basis of the above considerations it becomes difficult to propose a possible unique reaction mechanism.

It is well known that the formation of simpler organic products, originated at much longer irradiation times after the aromatic ring opening, occurs during the photocatalytic treatments. However, their identification was not examined since it was out of the scope of this reported preliminary study.

3.5. Effect of surfactants on the primary process kinetics

In order to investigate the effect of amphiphiles on the kinetics of swep degradation, photocatalytic runs were successively carried out in the presence of the investigated surfactants, at pH 5.6. The surfactant concentrations were the same employed during the soil washing experiments. The main scope of these experiments was the monitoring of the pesticide abatement and the corresponding results are shown in Fig. 6, where the swep degradation profile in water at pH 5.6 was included for comparison purposes.

A comparison of kinetic data obtained in water with that obtained in the presence of the three examined surfactants clearly indicates a more or less relevant inhibition of the photocatalytic process when performed in the presence of surfactants. The non-ionic surfactant $C_{12}E_8$ shows the highest inhibiting effect since only ca. 3.0% of initial substrate was degraded after 2 h irradiation at pH 5.6. For this surfactant, experiments at pH 3 and 8 were not further performed.
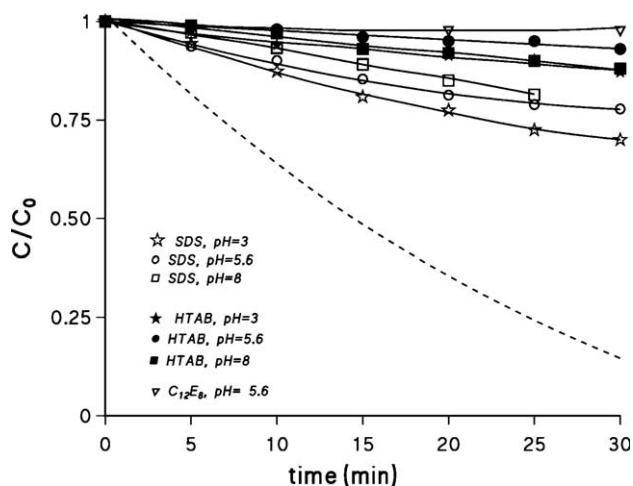

Fig. 6. Effect of surfactants on the evolution of the primary process during the photocatalytic abatement of swep. Dashed line: swep degradation profile in water at pH 5.6.

If the ionic surfactants are considered, the degradation was slower in the presence of HTAB. For both SDS and HTAB the degradation still fits a pseudo-first order kinetic law, but only up to approximately 25–30% of substrate conversion. From the examination of Fig. 6 it can be seen that the percent of swep abatement after 30 min irradiation, at pH 5.6, is around 22% in the presence of SDS and less than 8% in the presence of HTAB, whereas it reaches a value near 85% in pure water under the same conditions. After 120 min irradiation the degradation is still incomplete; for example, at pH 8, less than 29% of swep was degraded in the presence of HTAB, whereas more than 60% of the initial pesticide was degraded in the presence of SDS.

Some experiments have been also performed at surfactant concentrations below the corresponding c.m.c. values. The results (not shown here) are in agreement with previous findings reported in literature for other substrates. The observed inhibition effects are, as expected, lower under these conditions.

In order to further optimize the photocatalytic treatment, the effect of TiO_2 concentration and of air saturation on the process were investigated at a fixed initial pH (5.6) in the presence of SDS and HTAB. As reported in Table 2, an increase of the catalyst concentration until 1000 $mg\,L^{-1}$ raises the degradation rate, particularly in the case of SDS.

Moreover, a significant improvement of the degradation performances was also achieved by operating the saturation of the irradiated suspension with a bubbled air (flow rate ca.12 $mL\,min^{-1}$) through the reaction vessel. For SDS, in the presence of 1000 $mg\,L^{-1}$ of TiO_2, the observed swep abatement passes from ca. 80% to ca. 98% after 2 h irradiation.

The observed degradation enhancement was less neat for HTAB, for which a modest increase (from ca. 30% to ca. 34%) was, for example, observed when working in the presence of 600 $mg\,L^{-1}$ of TiO_2.

3.6. Degradation of soil washing wastes

On the basis of the above reported results, a set of experiments were performed on simulated soil washing wastes obtained by treating spiked soil samples with SDS. This surfactant was chosen on the basis of both extraction yield and kinetic degradation performances.

Therefore soil samples (94 g) were spiked with swep (24 mg) dissolved in acetone. After drying, the soil was extracted for 5 h with 625 mL of SDS 8.6 mM and 500 mL of soil washing extract were collected. The measured swep concentration in the extract was ca. 17 $mg\,L^{-1}$.

After centrifugation the supernatant waste was degraded in the reactor, in the presence of 1000 $mg\,L^{-1}$ of TiO_2, at pH 5.6, under continuous air flow. Samples of irradiated dispersion were taken at different irradiation times and analysed after filtration, as previously described. The complete disappearance of swep was achieved after ca. 6 h (see Fig. 7). The results are the mean of two replicated set of measurements.

The presence in the waste of other organic components coming from the soil leads to a slower degradation of the pesticide, if compared with previous findings obtained working with SDS in the absence of soil. However, even under these conditions, the photocatalytic treatment of the washing waste appears viable.

Table 2
Percentage of substrate abatement after 120 min as a function of TiO_2 concentration.

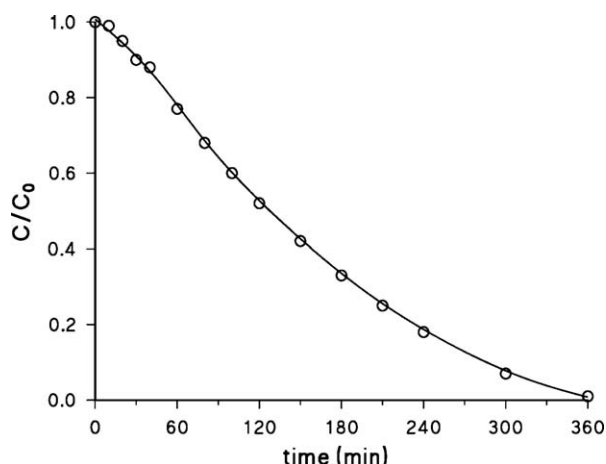|	HTAB			SDS		
TiO_2 concentration ($mg\,L^{-1}$)	200	600	1000	200	600	1000
% Abatement	19	30	30	35	47	80

Fig. 7. Photocatalytic degradation of swep in the soil washing waste.

4. Conclusions

The photocatalytic degradation of swep is relatively fast (within 50–60 min) in aqueous media under the examined experimental conditions. The HPLC-MS analysis of the organic compounds formed in water during the earlier degradation steps suggests that the simultaneous dechlorination and hydroxylation of the swep aromatic ring are the major initial routes of the process.

The presence of surfactants largely affects the degradation kinetics, however the treatment of surfactant-containing wastes arising from soil washing appears possible after a proper selection of the amphiphile. In particular SDS showed, among the surfactants investigated in this study, the best extraction efficiency of swep from contaminated soil samples. This surfactant also exhibited lower inhibiting effects on the pesticide photocatalytic degradation, thus suggesting its possible use for environmental remediation purposes.

References

[1] S.U. Khan, Pesticides in the Soil Environment, Elsevier, Amsterdam, 1980.
[2] W. Chu, W.S. So, Water Res. 35 (2001) 182–188.
[3] W. Chu, K.H. Chan, W.K. Choy, Chemospere 64 (2006) 711–716.
[4] W. Chu, K.H. Chan, Sci. Total Environ. 307 (2003) 83–92.
[5] Z.M. Zheng, J.P. Obbard, Water Res. 36 (2002) 2667–2672.
[6] L. Zhu, S. Feng, Chemosphere 53 (2003) 459–467.
[7] D.H. Lee, H.W. Chang, R.D. Cody, Geosci. J. 8 (2004) 319–323.
[8] K. Yang, L. Zhu, B. Xing, Environ. Sci. Technol. 40 (2006) 4274–4280.
[9] N. Serpone, E. Pelizzetti, Photocatalysis, Fundamentals and Applications, Wiley, New York, 1989.
[10] D.F. Ollis, H. Al-Ekabi, Photocatalytic Purification of Water and Air, Elsevier, Amsterdam, 1993.
[11] M.R. Hoffman, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69–96.
[12] S. Malato, J. Blanco, A. Vidal, C. Richter, Appl. Catal. B: Environ. 37 (2002) 1–15.
[13] H. Hidaka, S. Yamada, S. Suenaga, J. Zhao, N. Serpone, E. Pelizzetti, J. Mol. Catal. 59 (1990) 279–290.
[14] A. Bianco Prevot, E. Pramauro, M. de la Guardia, Chemosphere 39 (1999) 493–502.
[15] H. Tada, H. Matsui, F. Shiota, M. Nomura, S. Ito, M. Yoshihara, K. Esumi, Chem. Commun. 16 (2002) 1678–1679.
[16] D. Fabbri, A. Bianco Prevot, E. Pramauro, Appl. Catal. B-Environ. 62 (2006) 21–27.
[17] W.M. Meylan, P.H. Howard, R.S. Boethling, Environ. Toxicol. Chem. 15 (1996) 100–106.
[18] S. Deshpande, B.J. Shiau, D. Wade, D.A. Sabatini, J.H. Harwell, Water Res. 33 (1999) 351–360.
[19] J.-F. Lee, M.-H. Hsu, H.-P. Chao, H.-C. Huang, S.-P. Wang, J. Hazard. Mater. 114 (2004) 123–130.
[20] M. Muneer, D. Bahnemann, Appl. Catal. B 36 (2002) 95–111.
[21] A.G. Munoz, Electrochim. Acta 52 (2007) 4167–4171.
[22] C.R. Smith, K. Yaates, Canadian J. Chem. 50 (1972) 771–773.
[23] G. Alberghina, S. Fisichella, G. Musumarra, J. Chem. Soc., Perkin Trans. 2 (12) (1979) 1700–1702.
[24] M. Bergon, J.P. Calmon, J. Agric. Food Chem. 31 (1983) 738–743.
[25] K. Tanaka, S.M. Robledo, T. Hisanaga, R. Ali, Z. Ramli, W.A. Bakar, J. Mol. Catal. A-Chem. 44 (1999) 425–430.
[26] M. Bobu, S. Wilson, T. Greibrokk, E. Lundanes, I. Siminiceanu, Chemosphere 63 (2006) 1718–1727.
[27] E. Pramauro, M. Vincenti, V. Augugliaro, L. Palmisano, Environ. Sci. Technol. 27 (1993) 1790–1795.
[28] K. Tanaka, K.S.N. Reddy, Appl. Catal. B-Environ. 39 (2002) 305–310.
[29] Y. Oosawa, J. Phys. Chem. 88 (1984) 3069–3074.